

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) Jan 2014		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To) Jan 2014-Jan 2015	
4. TITLE AND SUBTITLE Peculiar Traits of Coarse AP			5a. CONTRACT NUMBER In-House		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Claude Merrill			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB, CA, 93524-7680			8. PERFORMING ORGANIZATION REPORT NO.		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Dr. Edwards AFB, CA, 93524-7048			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) <b>AFRL-RQ-ED-TP-2014-064</b>		
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES Technical Paper presented at JANNAF 46th CS / 34th APS / 34th EPSS / 28th PSHS Joint Subcommittee Meeting, Albuquerque, NM, 8 – 11 December, 2014.					
14. ABSTRACT Through various environments a factor influencing AP chemical activity is the propensity of coarse AP to produce porosity formation within its crystals. Porosity formation in coarse AP seems similar although at differing rates due to pressure and temperature influences in both isolated crystals and solid propellant combustions. Consolidated coarse AP crystals appear to be chemically unstable so that pure consolidated crystals cannot be made. Natural and accumulated trace impurities are responsible for observed porosity formation. In combustion environments kinetic action rates for coarse AP can be altered by materials on crystal surfaces and within the crystal bodies. Since orthorhombic crystal AP reaction rates are much faster in combustion environments than cubic crystal AP, orthorhombic phase AP is a primary actor during combustions. At very high pressures AP self combustion exhibits differential recession rates depending on whether surface regression is normal or transverse to the principal axis of its orthorhombic crystal structure. This behavior might be described as biaxial burning. Coarse AP oxidizer has observable chemical interactions that have not been observed for fine AP oxidizer during thermal decomposition and combustion environments. Coarse AP oxidizer has widely different chemical kinetic reaction rates between low and high heat fluxes. Widely different reaction rates are also observed between low and high pressure confinements. In solid propellants coarse AP promotes dark zone combustion, low burn rate pressure exponent, ease of burn rate adjustment, burn rate pressure exponent slope break, and slow cookoff violence.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Claude Merrill
a. REPORT  Unclassified	b. ABSTRACT  Unclassified	c. THIS PAGE  Unclassified			19b. TELEPHONE NO (include area code) 661-525-5169

# **PECULIAR TRAITS OF COARSE AP**

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## PECULIAR TRAITS OF COARSE AP

### ABSTRACT

Through various environments a factor influencing AP chemical activity is the propensity of coarse AP to produce porosity formation within its crystals. Porosity formation in coarse AP seems similar although at differing rates due to pressure and temperature influences in both isolated crystals and solid propellant combustions. Consolidated coarse AP crystals appear to be chemically unstable so that pure consolidated crystals cannot be made. Natural and accumulated trace impurities are responsible for observed porosity formation. In combustion environments kinetic action rates for coarse AP can be altered by materials on crystal surfaces and within the crystal bodies. Since orthorhombic crystal AP reaction rates are much faster in combustion environments than cubic crystal AP, orthorhombic phase AP is a primary actor during combustions. At very high pressures AP self combustion exhibits differential recession rates depending on whether surface regression is normal or transverse to the principal axis of its orthorhombic crystal structure. This behavior might be described as biaxial burning. Coarse AP oxidizer has observable chemical interactions that have not been observed for fine AP oxidizer during thermal decomposition and combustion environments. Coarse AP oxidizer has widely different chemical kinetic reaction rates between low and high heat fluxes. Widely different reaction rates are also observed between low and high pressure confinements. In solid propellants coarse AP promotes dark zone combustion, low burn rate pressure exponent, ease of burn rate adjustment, burn rate pressure exponent slope break, and slow cookoff violence.

### INTRODUCTION

AP has a room temperature orthorhombic crystal structure. When AP crystals are heated slowly to 240 C or more, a phase change to a cubic phase occurs. AP when heated under normal pressures to complete thermal decomposition does not exhibit a melting point (1). As expected for an ionic salt, lattice energy for AP is substantial, estimated as being -139.3 kilocalories per mole, kcal/mol (2). After AP transitions from orthorhombic to cubic phase at 240 C, crystal volume increases by 10.8%. That is, from a density of 1.95 grams per cubic centimeter, gm/cc, to about 1.76 gm/cc (3).

AP has varying combustion/decomposition modes. Fine and coarse AP react by different mechanisms in solid propellant. Since coarse AP in particles larger than about 150 microns are used in great majority for AP oxidized solid propellants, the nature of coarse AP in propellant combustion is an interesting subject (4, 5). Published investigations about AP thermal decomposition have provided insights into what is happening in coarse AP during combustion of AP oxidized solid propellants. Spontaneous hole productions (porosity) in coarse AP particles during propellant combustion influenced by high thermal flux and elevated pressure environments are greatly accelerated but similar to those observed in low temperature AP thermal decomposition studies. Coarse AP particles have a low temperature decomposition (LTD) behavior where holes emitting AP decomposition gases erupt from subsurface, reactive, impurity centers producing ellipsoids of revolution holes through the crystals (4,5,6). AP LTD has been observed to proceed in the temperature range of about 130 to 280 C (9). Five micron particle sized AP will not produce decomposition products by the AP LTD process at temperatures between 200 and 235 C while larger AP particles will (8). Coarse AP's combustion behavior in solid propellant has considerations having to do with time lapse delays needed for accomplishing phase change and pressure dependent induction periods or reaction hesitation before decomposition starts (4, 6). In a normal 10 mm per second (about 0.4 inches per second, ips) regressing solid propellant burn front time to traverse a 200 micron oxidizer particle from top to bottom would take about 20 milliseconds,

msec. If coarse AP does have a built in delay before combustion/decomposition traverses the depth of a 200 micron particle, times available for completing phase change or to get decomposition started would need to be some fraction of 20 msec.

AP decomposition is extremely variable exhibiting dependencies due to influences by temperature, pressure, level of impurities, fuel interactions, and particle size (4, 5, 6, 8, 11, 12). Combustion and decomposition processes for AP can take place at temperatures above 240 C directly from the orthorhombic phase because the speed of phase transition to the cubic phase is so slow that advancing burn fronts may move faster than the phase change process (4, 11, 12). Peculiarly, AP is less thermally stable as shown by differences in mass decomposition rates in the orthorhombic phase than in the cubic phase until temperatures reach ~300 C or more (6).

Kinetic burning rate of AP particles during propellant combustion may be modified by relative heat capacity of fine and coarse AP particles that have poor heat conductance. Fine AP particles, due to minimal heat capacity, in a receding propellant surface may heat up so quickly that nearly immediate reaction with adjacent binder material takes place. During most AP combustion processes of interest whether in propellants or non-detonating explosive events, coarse AP sites and associated porosity production play a discernable role. Rate of porosity production in coarse oxidizer during solid propellant combustion influences burn rates, burn rate pressure exponents, violence of slow cookoff trials, and even erosion rates under high velocity erosive burn recession conditions.

### **AP SELF DECOMPOSITION STUDIES**

Coarse AP's inherent propensity to form particle porosity was studied by Bircumshaw and Newman (4). After a coarse AP weight loss of about 30%, the remaining material was high purity AP with a porous structure. During the AP LTD process at temperatures ranging from about 200 to 280 C, a time delay of a few minutes to more than half an hour was observed. Such time delays before AP gaseous products emissions were called induction periods. Their AP thermal decomposition studies were conducted in a wider temperature range 200 to 450 C, but the AP LTD process was the most interesting. Once started, AP LTD gassing rate was much faster at 230 C rather than at 245 C. Since AP's phase change temperature is 240 C, decomposition kinetics close to that temperature were faster in the lower temperature stable orthorhombic crystal phase than in the upper temperature stable cubic phase. Within coarse AP particles they observed microscopic, cloudy particles that could coalesce into larger, but still quite small reaction centers. Holes into coarse AP particles started at subsurface reaction centers that were observed as cloudy spots under microscope observation. Such holes or pores were sources of AP decomposition products. Numerous materials from both cocrystallized and external vapor exposures typically changed AP LTD decomposition rates or induction periods.

Although AP and products for AP decomposition are colorless, the nuclei and reactive centers were readily observed visually. This likely arose due to the difference in index of refraction between AP crystals and impurities forming nuclei in the orthorhombic crystals.

Gassing rates and extent of AP decompositions were observed to vary with AP particle size. At a temperature of 230 C, Bircumshaw and Watson (5) found that particles giving the fastest thermal decomposition rates were in the 100 to 200 micron size range. Smaller and larger particle size oxidizer gave lower mass losses before stopping decomposition in AP LTDs. They noted that in the temperature range of about 200 to 270 C ~200 micron particle sized AP decomposition could proceed to ~30% weight loss and then stop leaving very porous AP residues. At higher temperatures noticeable AP sublimation

vapor pressures occurred. AP sublimed vapors were produced by disassociation into perchloric acid and ammonia that can readily recombine to regenerate AP.

Raevskii and Manelis (6) undertook to investigate the character of the large particle AP LTD process. That is, at temperatures less than 240 C. Microscopic observation of heated crystals could see clouds of small about 1 micron particles they described as nuclei. These nuclei were nonuniformly distributed, but moved and joined up to form reactive centers. Reactive centers grew to a maximum size of about 2 microns and ceased to grow. Microscopic amounts of liquid containing water were contained in the reactive centers. The maximum size for reactive centers was reasoned to be inhibited by local rising water content from AP decomposition. At 234 C nuclei had maximum linear velocity along the main orthorhombic crystal axis in the range of 7 to 10 microns per minute. Smaller nuclei moved faster than larger ones. Activation energies for nuclei movement were determined as being 31 kcal/mol along the orthorhombic crystal longitudinal axes and 33 kcal/mol in the transverse direction. Transverse velocity of nuclei was roughly about one tenth that along the main orthorhombic crystal axis.

After some delay at temperatures of about 235 C, linear holes were observed to form parallel to the major axis of the orthorhombic phase. Decomposition gases were emitted when larger centers produced surface dents that became sites of gas emitting holes extending into AP crystals. These holes were described as cigar shaped or ellipsoids of revolution where central diameters were larger in the middle of the pores than at either ends. Holes were observed as originating from elongated reactive centers parallel to the main orthorhombic crystal axis. Reactive centers were subsurface and a few microns in depth. Internal pressures in the reactive centers were estimated as being around  $2 \times 10^6$  Pascals, ~twenty atmospheres pressure. Internal pressures dictated that shallower nuclei in bursting out of the AP crystals might destroy evidence that surface nuclei ever existed. Visible reactive centers were estimated as being about 3 microns or more in depth to have adequate AP crystal strength to prevent bursting out from internal pressure. These reactive centers were observed to produce ellipsoid holes of revolution formation after some delay at temperatures below the AP 240 C phase change temperature. Raevskii, Manelis, Boldrev, and Votnova (7) reported that maximum pore density in ~200 micron size crystals was estimated as being in the order of  $10^6$  per square centimeter,  $\text{cm}^2$ .

A breakthrough in understanding of reactive centers nature in AP was been provided by Khairetdinov and Boldyrev (8) in recognizing that the centers contained ammonium chlorate and some amounts of AP degradation products. Khairetdinov and Boldyrev called small nuclei "seeds or germs". They observed joining of germs into larger centers. They called growth of larger centers auto-localization. Activation energy for nucleation was determined as being about 70 kcal/mol for high purity AP and about 50 kcal/mol for chemically doped AP. Rate of AP decomposition products formation increased as germs grew to larger sizes. Increased concentration of chlorate ion in AP produced a proliferation of germs and decreased induction time before AP LTD process started. A proliferation of germs resulted in increases for gas evolution rates. Changes in induction time reduction and increases in rate of AP LTD reactions were chlorate ion concentration dependent. As chlorate content was increased decomposition reaction rates were greater in the AP LTD process.

Efforts to take out chlorate ion completely failed. AP produced from high purity samples of ammonia and perchloric acid produced AP having a reduced concentration of chlorate ion content. Higher purity AP exhibited slowed AP LTD gassing rates and increased induction periods before AP decomposition commenced. After conducting recrystallization of the high purity AP five times, they came to the conclusion that consolidated, crystalline AP is fundamentally unstable with respect to always producing a minute amount of ammonium chlorate impurity. At the lowest chlorate content in their

recrystallized AP, migrating nuclei and germ growth at low concentrations could still be observed despite their chemical analysis method being unable to detect chlorate content. Khairatdinov and Boldyrev noted that 5 micron sized AP crystals did not show any tendency to decompose by the AP LTD. This inertness was caused by the requirement for the AP LTD to have active pore producing sites at a minimum of about 3 microns depth within AP crystals. Boldyrev (9) noted in his latest review of AP thermal decomposition that ammonium ions in an AP crystal are freely rotating in both orthorhombic and cubic crystal phases, but that perchlorate ion is not free rotating in the orthorhombic phase but is free rotating in the cubic phase.

AP decomposition investigators did not propose a mechanism for germ movement through AP crystals. A difficulty in rationalizing center movements is, "How can chlorate ion only a little smaller than perchlorate ion size push through a crystal structure that is tightly bound by ionic forces?" Since AP has a large lattice energy, 138.3 kcal/mol (2), energies required to physically move chlorate ions,  $\text{ClO}_3^-$ , past perchlorate ions,  $\text{ClO}_4^-$ , in three dimensions must be very large. Energy for shouldering aside perchlorate ions could be larger than chemical bond strengths in the ammonium perchlorate chemical structure. According to Raevskii and Manelis, activation energies for longitudinal and traverse nuclei movements were 31 and 33 kcal/mole, respectively (7). Such activation energies are too weak to directly move chlorate ions through the AP chemical structure. A more likely explanation for migrating nuclei would be for chlorate ions taking an oxygen atom from an adjacent perchlorate ion converting the oxygen donating perchlorate ion into a chlorate ion that was a perchlorate ion width away from the original chlorate ion. Net energy for the oxygen atom exchange process should be zero since energy of breaking an oxygen atom to chlorine atom bond in a perchlorate ion would be balanced by heat evolved by forming a new oxygen atom to chlorine atom bond in the original chlorate ion. Oxygen atom swapping between chlorate and perchlorate ions would provide chlorate migration without use of forces capable of disrupting the AP crystal structure. Energy difference between lattice energies for AP ions versus lattice energies within the germ nuclei could be a driving force favoring consolidation of chlorate ion rich domains. That perchlorate ions in the AP orthorhombic crystal structure are not freely rotating (9) may contribute to ease of oxygen atom transfer. Greater ease of oxygen transfer in the AP orthorhombic structure may explain the large kinetic difference in AP decomposition between 234 C and about 244 C. At a 244 C temperature, that is above the AP crystal phase change temperature, free rotation of perchlorate ions could serve to inhibit oxygen atom transfer.

AP crystals may have variable phase change temperature. Since AP transitioning from orthorhombic to cubic phase increases 10.8% in volume (3), applied pressure would try to counteract the phase transition. Examples are rare that could help grasp how much AP phase transition temperature might increase by application of enhanced pressures. Although a poor analogy, HMX is known to have a crystal phase change temperature that rises due to applied pressure. HMX phase change point increases in temperature by about 30 C per kilobar pressure (10). One kilobar pressure is equivalent to about 14,500 psi. Volume change increase by the phase change was about 6.3%. By simplistic analogy AP might have a phase change temperature rise of, perhaps, 50 C per kilobar of applied pressure.

### **AP SELF-COMBUSTION**

Self-combustion of large AP crystal cleaved sections was studied by Thom Boggs (11, 12). With a window equipped combustion bomb Boggs took movies of AP crystal burning. His crystal samples were about 5 by 5 millimeters by 1 millimeter thickness. Combustion initiation was started by electrically heated Nichrome wires. With AP crystals mounted in relatively massive copper jaws AP crystal combustion quenched due to thermal losses as crystal burning came near jaws area allowing

examination of recovered surfaces that had been burning. Bogg's combustion bomb allowed combustion experiments ranging from about 300 psi to 6200 psi. Character of the recovered, flame quenched surfaces changed dramatically over the pressure range investigated.

Thom Boggs observed that large AP crystals would burn with little, if any, contribution by the AP cubic phase since he could see non burning material being pushed off an AP burning surface that was receding. His observations demonstrated that AP phase change was a relatively slow process, even when combustion was conducted at pressures of 500 to 1000 psi. Cubic phase AP thickness on flame quenched surfaces was thin and became thinner as chamber pressures were increased along with pressure enhanced burn rates. Recovered, fire quenched, AP crystals showed undercutting of cubic phase AP left on top of a formerly burning orthorhombic phase surface. These observations demonstrated that orthorhombic phase AP burned at a faster rate than for cubic phase AP.

Boggs found that pure AP would not sustain a flame at pressures lower than about 300 psia. AP burning behavior could be readily divided into four pressure range sections. In pressure region I between about 350 and 800 psi a steady, positive, burn rate pressure exponent was exhibited. Pressure region II in about the 800 to 2000 psi range had a positive, burn rate pressure exponent that was gradually declining. Near 2000 psi an abrupt change to a strongly, negative, burn rate pressure exponent set in that had lessening negative exponent until bottoming out near 4000 psi. The negative exponent 2000 to 4000 psi range was called pressure region III. At about 4000 psi in pressure region IV the burn rate pressure exponent reversed at increasing pressure to positive values increasing to exceed exponent values well above 1.0. The high exponent trend continued up the test limit of about 6200 psi. Cleaved AP crystals burned fairly evenly at pressures near 1000 psi. However, AP crystals burned quite unevenly in the 2000 to 4000 psi pressure range III.

In region I bubbling was noted during AP crystal self-combustion. Region I AP crystal burning was relatively planar. A white froth, assumed to contain recombined sublimed AP completely covered quenched surfaces upon completion of an experiment at about 300 psi. Sublimed AP would be expected to be a mixture of ammonia and perchloric acid that could produce a main ingredient of observed AP froth by chemical recombination. Part of the froth at low pressures could have been fragments of less reactive, cubic phase AP. On flame quenched surfaces white froth about 1 to 5 microns thickness was on top of a thin skin AP cubic phase layer resting on remaining orthorhombic AP crystal. As experimental pressures were increased, the amount of froth declined until at 800 psi white froth residues were patchy. Fragile froth material may have included entrapped liquid (water based) and gas material. Holes were observed in low concentration with raised edges as if liquid had erupted from within the AP crystal. Some holes were larger than 20 microns in diameter with unmeasured depths below quenched crystal surfaces. Profiles of quenched surfaces in region I indicated some surface roughness.

Bubbling largely disappeared in Boggs' AP burning trials in pressure region II, 800 to 2000 psi. Early in pressure region II froth disappeared. Some craters were observed in a few of his photos. Quenched surfaces were considerably rougher than seen in pressure region I. Some recovered surfaces exhibited patterns of parallel ridges and valleys. With pressure increases in region II AP appearance of cubic phase diminished. Some sloughing away of ridges without apparent burning as burning crystal surface regressed was noted. AP cubic phase was thicker on the ridges than in the valleys. At 1800 psi cubic phase thickness in the valleys was about 3 microns while cubic phase thickness on ridges was about 30 microns. Some isolated pockets of AP needle residues were noted from trials at 1500 and 1800 psi.

AP crystal burning in pressure region III was very unsteady with respect to non-uniformity of regression and shifting of flamlets above the regressing surface. No measurable AP cubic phase remained after quenching of crystal burning. Surface regression occurred under visible flamlets, but adjacent areas seemed stationary for some periods. When flamlets shifted to formerly stationary areas, those areas regressed. Quenched surfaces from AP burning at 3300 psi in the region of maximum regression had pockets of vertically standing, irregularly shaped rods of AP. A number of residual rods were curved as if they were sections of tubes.

Flame observed in pressure region IV, 4000 to 6200 psi, was in contact over the entire regressing surface. This was in contrast to region III tests where flame movements oscillated unevenly over regressing surfaces. Photos of quenched crystal surfaces showed needle residues covering the entire surface. Needles in region IV extended from the surface about 150 to 200 microns. These needle remainders were about the same size as found in isolated pockets in pressure regions II and III.

Boggs' photographic data showed apparent changes in AP burning as combustion bomb environmental pressures were varied from about 300 to 6200 psi. AP porosity formation during his experiments might have been playing a role during in all of the experiments but to a different degree as AP self-combustion was observed in his pressure regions I through IV (11, 12). In pressure region I the observed, widely spaced large holes could indicate bursting out from larger active centers with high internal pressures as indicated by Raevskii (6). Large active center originated pores was a minor part of the of the AP crystal burning process in pressure range I. Principal part of the combustion could be coming directly from AP orthorhombic phase and/or, multitudes of small gas jetlets as receding, burning crystal surface encountered small germs. At low pressures froth suspended by minor jetlets or other gas emissions could contribute to the observation of bubbling. Mechanical forces from a high pressure pocket burst could provide lifting of pore peripheries. Amount of liquid involved could have been minor since amount of water liquid content in Raevskii's active centers was quite small (6). Slow burn rates in pressure region I evidently were slow enough that some degree of phase change to cubic phase AP could take place. Froth levitated by gases from the surface below could have been mixture of AP decomposition product gases, recombined AP from gaseous sublimation of AP, and fragments of cubic phase AP nearer to the regressing AP crystal surface. Since AP regression rate increased with pressure, reduced time for AP cubic phase formation on recovered crystal surfaces following quenching would logically diminish as was observed with increasing experimental pressures.

In some of Boggs' pressure region II photos (11, 12) a dramatic change was observed when comparing quenched surfaces recovered from AP crystal burning with those received from pressure region I. Irregularly aligned parallel ridges and valleys were obtained in contrast to relatively flat quenched burning surface punctuated by occasional pores seen from pressure region I trials. Froth had largely disappeared and cubic phase AP coating was thinner although cubic phase thickness diminished with increasing pressure in pressure region II. Since cool down upon crystal quenching was a relatively slow process, Boggs' observed amount of cubic phase likely increased in thickness following the flame quenching process. Boggs' measurements found cubic AP thicknesses at top of ridges to be about 30 microns and at valley bottoms to be about 6 microns. Seemingly, a completely different combustion mechanism was involved. Boggs' had quenched surface pictures at 1200 and 1800 psi that clearly showed surface holes, but area surrounding the pores did not have discernable ridges and valleys.

Raevskii observed that hole formation initiated from his active centers had a preferred crystal orientation. Gas product emitting holes bursting out of crystals by the AP LTD process formed exclusively parallel to the primary orthorhombic crystal axis (6). What would happen if some of Boggs' cleaved AP



crystal burns were initiated so that surface recession proceeded orthogonal to the principal orthorhombic crystal axis?

Since AP orthorhombic crystals are naturally longer in one direction, Boggs' cleaving of AP combustion samples from large crystals could often be cleaved along the longest crystal dimension. Sample sizes were said to be about 5 mm square. In the absence of knowledge of AP hole forming chemical reactions having preferred chemical reaction rates parallel to the long axis of the orthorhombic crystal Thom Boggs may have tested some of his cleaved samples (11, 12) in orientations with regressing surfaces being split between being orthogonal and parallel to the main orthorhombic crystal axis. Although propagating combustion was not observed at low pressures, Raevskii and Manelis' (6) ellipsoids of revolution indicated a substantial differential in AP chemical decomposition rate between material loss parallel to the orthorhombic crystal main axis extending pore length and lateral chemical reaction losses that would enlarge pore diameters. Further, their determination of activation energies for movement of mobile germs indicated that movement parallel to the crystal main axis had an activation energy of 31 kcal/mole while lateral movement orthogonal to the crystal main axis had an activation energy of 33 kcal/mole. Activation energy bias for the chemical process of germ movement might operate similarly during AP crystal self combustion. If an AP sample cleaved from an orthorhombic crystal was positioned such that the major crystal axis was parallel to the regressing surface during a burn trial, intermittent activation of a Raevskii and Manelis (6) active center could produce parallel troughs where elongation of the trough would be much faster than recession rate of the burning surface. What was a very narrow crystal hole in Raevskii and Manelis' less than one atmosphere pressure AP decomposition experiments would logically burn outward at many atmospheres pressure in a semicircular fashion at a high rate as activate sites were triggered to participate in the AP combustion process. Parallel ridges and valleys observed from tests in pressure region II (11, 12) could be interpreted as operation of the AP hole forming process with the primary orthorhombic axis orthogonal to the direction of burn front recession.

With a strong negative burn rate pressure exponent for AP combustion in most of Boggs' (11, 12) pressure region III something unusual was taking place in the gas phase that inhibited the AP hole forming process. AP crystal regression at 4000 psi was decreased by about 98% with respect to regression rate at 2000 psi. Ammonia is known to majorly inhibit AP decomposition in the orthorhombic phase and totally inhibit AP cubic phase decomposition (4). If gas phase reaction mechanisms for sublimed AP decomposition changed dramatically with pressure, a result might be that a surplus amount of ammonia in the gas phase could be produced. If a gas phase surplus of ammonia during high pressure, 2000 to 4000 psi, occurred during AP decomposition, great inhibition of rate of AP decomposition could be expected. Nonetheless, flamlets jumped around during AP burn trials in region III and some sites were activated into AP decomposition preferentially as compared to others. Flame outbursts took place sporadically. During region III AP burn trials, one side of AP orthorhombic crystal sample surfaces regressed several times faster than in the least regressed areas. Appearance of vertically standing parallel, irregularly shaped, AP rods at the site of maximum regression appeared as evidence for operation of the AP LTD (hole generating) process with the primary orthorhombic axis aligned parallel to the direction of burn surface recession. A substantial number of the rods appeared as fractional remains of tube walls. If fast recession rate, deepening hole enlarging porosity was activated at multitudes of sites as compared to those in pressure region I tests, remaining elongated, curved shards would remain after slower outward regressing decomposition sites merged into each other. AP rod residue formation in pressure region III could come from AP sporadic orthorhombic phase LTD process.

In Boggs' pressure regions III and IV quenching left standing AP needles that could be described as formed by similar, very accelerated rate AP LTD processes as observed at very low pressures.

Raevskii and Manelis (6) noted in their low pressure test environments that LTD process formed hole extensions several times faster than width expansion of their ellipsoids of revolution. This same general trend with much accelerated AP LTD process seems to have been operating at Boggs' high pressure AP crystal combustions. In pressure region IV the burn rate pressure exponent may have reached a value as high as 3.0. Holes proceeding into AP crystal depths faster than lateral regression of the holes leaving linear wall fragments of ellipsoids of revolution upon quenching seems to explain the formation of the column residues at highly elevated pressures. Such a reaction rate disparity based on crystal axis orientation might be called bidirectional burning.

## **SOLID PROPELLANT COMBUSTIONS**

Most of the propellant examples covered in this section will be HTPB and CTPB/AP compositions with or without Al. One example used an energetic binder as an aid for getting very fast propellant burn rates.

During the period that Dr. Richard M. Miller, Chemical Systems Division of United Technologies, was conducting combustion experiments at Edwards AFB, CA, 1981-2, he mentioned that he had observed frequent coarse oxidizer ejections during window bomb solid propellant combustion tests. His propellants were variations of a reduced smoke, HTPB/AP, propellant. Further description was that the propellant contained 87% total solids, and that coarse oxidizer, 200 micron AP, mass fraction was above 40% of propellant content. Fine fraction AP in Dr. Miller's propellants had particle size of about 2 microns. His observations were conducted in propellant burning trials contained in a combustion window bomb. Propellant recession events were recorded by a camera operating at 1000 frames per second. Substantial magnification aided seeing small details on receding propellant surfaces. Combustion trials were often carried out at nitrogen gas pressures of 2000 psi. With Dr. Miller I observed a few of his movies played back at about 25 frames per second (13).

During Dr. Miller's 1000 frame per second combustion bomb movies, individual coarse oxidizer particles would loom up out of the receding propellant binder rich surface for a few frames followed by abrupt disappearance of single particles within the duration of a single frame. Lack of aluminum in the propellants being tested eliminated bright burning aluminum agglomerates that would otherwise mask seeing details of coarse oxidizer particle behavior during propellant burn sequences. Fine AP oxidizer of about 2 micron particle size having very short lifetime as propellant surface regressed also contributed to ease of watching 200 micron AP activity. In the spot where a coarse oxidizer particle abruptly left remained a rounded cavity within the binder rich surface that shortly disappeared with burning front recession. Minimal immediate enlargement of vacated binder cavities was noted. Although Dr. Miller had said that large oxidizer particle ejection was frequent, I observed universal coarse particle ejection. Nowhere did I see evidence of flame at the periphery of large oxidizer particles where they contacted with the binder rich part of the solid propellant. Claiming universal 200 micron AP particle ejection would be statistically risky since I only observed relatively few oxidizer particles in the combustion movies reviewed.

Under 2000 psi combustion at 0.4 inch per second, ips, propellant surface recession rate would be close to 10 microns per millisecond. If a 200 micron sized oxidizer particle would remain in place, time to traverse from the top of a 200 micron AP particle to its bottom would take 20 milliseconds. Although the number of frames where individual coarse oxidizer particles would be visible was not counted, it seemed to be about 4 to 5 frames. Thus, time delay of coarse AP particle visibility would be about 4 to 5 milliseconds. The delay before visible evidence of AP particle action raises interesting thoughts.

How did 200 micron AP particles last for several milliseconds in a high heat flux environment and then disappear fairly abruptly? A point of contrast is that AP has lower long term thermal stability than for the HTPB propellant binder. The low thermal decomposition temperatures recorded by AP investigators was based upon long duration observations at various temperatures, generally, at temperatures less than about 450 C (4). Those observed low temperature AP decompositions originating from active centers within AP crystals always had considerable induction period delay before gas evolution took place, as least minutes (4, 6, 8). With an induction period before AP thermally decomposes, oxidizer particles seem to have robust, though fleeting, thermal stability in high heat flux environments. Boggs noted that at AP cleaved crystal burn rates in the order of 0.5 ips AP that phase transition from orthorhombic to cubic phase occurred in limited amount (11, 12). Coarse oxidizer domes emerging from the receding binder rich propellant surface may have adequate time under a high heat flux environment to start phase transition at the top of the particle dome. Markowitz and Boryta reported that AP crystals in transitioning from the orthorhombic phase to the cubic phase increase in volume by 10.8% (3). AP has quite low thermal conductivity. An exposed large AP particle dome skin in a high heat flux environment would get heated rapidly while particle core temperature would lag behind the surface temperature. Elevated temperatures for a thin skin of a coarse oxidizer particle dome could result in few millisecond time periods before phase change started. While transitioning AP phase change, the heated, thin skin on coarse particle domes would be subjected to strong compressive forces. When thin skin mechanical failure occurred, rapid reactivity for exposed, subsurface, reactive sites could be triggered with holes rapidly propagating completely through the oxidizer particle. With a multiplicity of triggered ellipsoid of revolution diameter pore enlargements through AP decomposition at high pressure conditions, a mild forced explosion of the oxidizer particle into a combination of gas and, perhaps, small solid particles could take place. This large oxidizer particle popping scenario may be a probable explanation for the rather abrupt disappearance of coarse oxidizer particles after they emerged from the binder rich portion of the propellant.

Coarse AP oxidizer temporary flame retardant character exhibited in combustion window bomb observations for reduced smoke propellant was surprising. Time delay before chemical activity for coarse AP oxidizer begins may be a contributing factor to why many slow burning propellants have low burn rate pressure exponents in the range of 0.3 to 0.45. Slow burning propellants may have their burn rates controlled largely by coarse AP oxidizer short term flame retardancy. AP flame retardancy character may have its source in extended time induction periods for chemical decomposition to start as noted by earlier investigators observations for the AP LTD process (4, 6, 8, 9). Trading out some coarse oxidizer for added ground oxidizer is a ready method for adjusting propellant burn rate to a higher value. In solid propellants having coarse oxidizer contents above 40% by weight introduction of finer ground oxidizer seems to have only marginal effect in raising propellant burn rates. However, altering AP coarse to fine particle size ratio regularly produces immediate, predictable burn rate changes. This leads to the thought that changing magnitude of coarse oxidizer flame retardancy may be the most effective way to adjust many solid propellant burn rates.

Time delay for coarse oxidizer particle disintegrations followed by formation of brief, punctuated bursts of oxidizer gases mixed with oxidizer particulates leaving burning propellant surface could contribute a space of poorly mixed fuel and oxidizer that would be a dark zone above propellant receding surfaces. Dark zones can be most easily observed during window bomb combustion at low pressures. Above the dark interval closest to burning propellant surface turbulent mixing with AP particulate vaporization would provide intermixing with fuel materials that would blossom into an incandescent bright zone.

Small oxidizer particles may be produced during coarse oxidizer particle ejection along with AP decomposition gases. If AP LTD porosity generation takes place, only immediate fractional conversion to gas may take place according results by AP decomposition investigators (4, 6, 8, 11, 12). Estimated monopropellant flame temperature for AP at 1000 psi is about 1400 Kelvin. If coarse AP particles during ejection provided complete, immediate combustion as they were leaving a cavity, thermal heat transfer could be expected to provide almost instant combustion recession of the cavity. This was not observed. Since interior of a partially exposed coarse AP particle would be at temperatures vastly below that of the propellant combustion, fractional, relatively immediate mass conversion would be logical. Lack of immediate coarse oxidizer cavity recessions and luminous flame in ejected coarse AP cavities supports the concept that small particulate AP ejection could be involved. Particulate expulsions of ejected coarse AP could help to contribute to temporary poor oxidizer and fuel mixing that would encourage dark zones close to receding propellant surfaces during combustions.

How would coarse AP particles after going through the AP LTD process with a weight loss roughly between 18 and 35% work in a solid propellant? Edwin L. Lista (14) at Aerojet facilities studied use of porous AP oxidizer in CTPB, polyether, polyester, and acrylate binders to make solid propellants. He made porous AP by putting shallow layers of propellant grade 200 micron sized AP into stainless steel trays and putting them in an oven at 265 C for 30 minutes. The porous AP was physically weak, cracked, and full of holes. One of Lista's porous APs had a particle density of about 1.5 gm/cc and a bulk density of about 0.85 gm/cc. When formulated into solid propellants, burn rates were greatly increased as compared with propellants in the same binder system using full density coarse AP oxidizer. Propellant burn rates were highest when porous AP particles were heavily precoated with a polymer of propylene imine adduct of divinylbenzene. One of his examples used 3% coating on the porous AP. A burn rate of 3.5 ips at 2000 psi was obtained for one of his CTPB propellants. Burn rate pressure exponent for that propellant was 0.6.

Porous AP was never used in any fielded system. Lack of thrust performance was a principal problem since porous AP density dictated that any pourable blend for propellant grain fabrication required much more binder volume to get a suitable volume ratio of liquid to solids to obtain pourable viscosity. Reduced total solids, porous AP propellants were lower in density and specific impulse than conventional solid propellants. These factors guaranteed that propellant boost performance was low. Since porous AP particles were very fragile, low viscosity was needed throughout propellant mixing operations to limit particle fracturing. Attempts at higher solids loadings resulted in differing batch to batch burn rates (14).

When low burn rate solid propellants oxidized by AP reach high pressures, typically at some point above 3000 psi, burn rates increase dramatically. Burn rate pressure exponents up to values of 1.6 have been above 3000 psi. Start of rather abrupt increase in burn rate pressure exponents have been called "slope breaks." Coarse AP oxidizer sizes above 150 microns are responsible for solid propellant slope break behavior at pressures in the ~3000 to 12,000 psi range. With 200 micron sized coarse AP oxidizer in large proportion of solid propellant formulation slope break shift can take place at about 5000 psi. Analogous propellant utilizing 400 micron sized oxidizer can result in a slope break at about 3000 psi (15). Analogous propellant using 90 micron sized (measured as 78 microns) AP coarse oxidizer did not show any abrupt slope break at any pressure up to 60,000 psi according to Lawrence Livermore National Laboratory's Dr. John Maienschein (16). With the 90 micron sized AP oxidizer propellant, burn rate pressure exponent increased gradually above 10,000 psi until an exponent of 0.9 was attained at 30,000 psi. Slope break transition pressures are influenced by oxidizer impurities. As coarse oxidizer content is lowered, threshold pressures at start of burn rate pressure exponent slope break shift increases.

A former goal for the Propellant Laboratory at Edward's AFB was to develop a solid propellant having a 10,000 psi burn rate of about 10 inches per second. Initial formulation efforts were to make a series of propellant formulations containing a trimodal AP oxidizer blend of 2.2, 16.7, and 200 micron sized particles. In successive propellant trials in small 2x4 motors, using propellant grains 2.0 inches outer diameter by 4.0 inches long, 200 micron AP content was incrementally reduced to 5% by weight. Propellant slope break pressure rose as 200 micron oxidizer content was diminished. At 5% 200 micron AP content the slope break pressure had only risen to 7200 psi from 5000 psi. In addition, propellant burn rate remained far short of the burn rate goal. Totally removing 200 micron AP oxidizer from the propellant formulation and going ahead with a bimodal blend of 2.2 and 16.7 micron oxidizer, gave a large jump in propellant burn rate. Measured propellant burn rate at 10,000 psi was slightly above 10 inches per second. Motor firings were conducted up to 13,000 psi without observing any burn rate pressure exponent slope break.

Below in Figure 1 is given a plot of burn rate versus pressure for an 88% total solids HTPB/Al/AP solid propellant. Oxidizer particle size blend was a mixture of 200 micron particles and ground oxidizer prepared from the available lot of 200 micron sized AP. Amount of 200 micron AP was 50% by weight in the propellant formulation. Burn rate at 1000 psi was near 0.32 ips. First slope break occurred near 5000 psi with an exponent of 1.6 and a second slope break down to a burn rate pressure exponent of 0.9 took place at about 12,500 psi (15).

Why should coarse AP oxidized solid propellants have burn rate pressure exponent slope breaks? Elevated burn rate pressure exponent values above slope break pressures, usually greater than one starting variously in the region of 3000 to 5000 psi, are similar to AP self-combustion burn rate behavior in pressure region IV reported by Thom Boggs (11, 12).

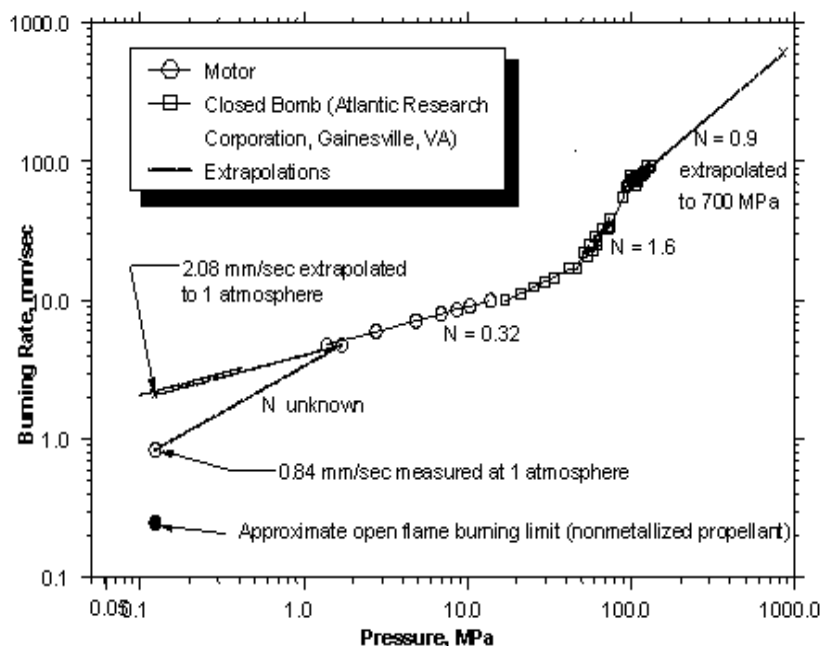


Figure 1. Burn rate versus pressure for HTPB/Al/AP propellant having 1000 psi rate of 0.32 ips

Original notice of AP porosity producing activity in AP particles larger than 100 microns size was in finding that holes penetrated through AP particles starting at visible active centers (4, 6). These holes

had crystal axis directionality. Hole diameter enlargement took place at a slower pace than hole extension. It seems that the AP porosity forming mechanism plays a part in differing proportion and at widely differing rates during all thermally induced methods for coarse AP particle chemical reactions. Induction periods for large AP particle decompositions vary from many minutes at one atmosphere pressure to, perhaps, fractions of milliseconds during combustion processes at pressures above about 5000 psi pressure. As higher heating and heat transfer rates are exerted, AP combustion typically takes place exclusively from its orthorhombic crystal phase, mainly due to faster surface regression with short duration for uncovering AP particles in a receding burn front. At pressures below 1500 psi the large particle AP LTD process can play a minor role as in Boggs' AP crystal self-combustion since AP had reluctance to start porosity formation due to induction delay periods. In solid propellants oxidized with large AP particles, high thermal heat flux on exposed AP particles combined with phase change volume expansion can short circuit induction periods. Coarse AP particle ejections may start as thermomechanically induced AP particle fracturing atop exposed particle domes. Mechanical breaking of AP particle domes will expose many of the about 3 micron depth active sites dispersed within the AP crystal. Once induced large AP particle fracture takes place, exposed active sites may quickly propagate holes through particle bodies with nearly immediate fractional AP particle gasification and fragmentation. Visibly at millisecond durations the process would appear as coarse particle ejection. Seemingly, as combustion pressures increase, ease of starting hole porosity seems to become enhanced. As pressures rise between ~4000 psi to 12,000 psi changes in burn rate could be considered as an increasing proportion of hole forming activity in coarse AP oxidizer to the point where complete saturation of the mechanism occurs. For the example provided in Figure 1 saturation of the hole forming porosity process has taken place at about 12,500 psi. Fire through a profusion of holes in large oxidizer particles may even produce exploded particles that would accelerate propellant burn rate despite variable orientations of crystal axes. Transfer of fire from top of 200 micron AP particles in propellant to the bottom of the AP particles on the average evidently can occur faster than the natural tendency of propellant regression through binder rich proportion of propellants than expected during normal rocket propellant combustion. In over 5000 psi conditions fire can be transferred to the bottom of AP cavities to prompt immediate fuel rich binder burning since heat transfer can be quite fast due to the 1400 K AP monopropellant flame and high gas densities.

Burning of propellant at 12,500 psi as in Figure 1 erupting coarse oxidizer particles can no longer increase fire transmission further ahead of the normal binder recession rates. That is, burning rates cannot continue at a burn rate pressure exponent above one. At that pressure level burn rate pressure exponent at even higher pressures remained constant at about 0.9 (14).

In slow cookoff trials for rocket motors filled with PBAN, CTPB, or HTPB propellants oxidized by coarse AP porosity will add to violence of the end of the process. Since slow cookoff tests use a heating rate of 6 F increase per hour, many hours at elevated temperature pass before spontaneous combustion of propellants within motors begins. Long time duration at elevated temperatures is favorable for getting the AP LTD process to take place. Porous AP will be produced from coarse oxidizer particles. Porous AP in propellant has been recognized as a way for obtaining very high propellant burn rates (14). Not only will gas bubbles from AP decomposition accumulate, but fuel components, such as, plasticizer and initial binder decomposition products can get into generated AP pores allowing intimate contact between fuel and oxidizer. Such a porous, bubbly, intimate oxidizer/fuel mixture is a prescription for an explosive event. Part of the problem with end of slow cookoff rocket motor trials is the motor case containment factor. With a fixed nozzle aperture any propellant combustion mass flow rate above some value will be expected to readily burst motor cases. Even filled with hot non-reacting gases motor case bursts will be

violent. The situation where propellant combustion is contributing to slow cookoff motor eruption violence makes the event stronger.

Mr. Dan Meyer, Aerojet, Sacramento, CA has detected that purity of coarse AP oxidizer in an HTPB booster propellant affects the rate of propellant erosive burning. In a motor exhibiting erosive burning during early stages of motor firing, Dan determined that higher chemical purity of the coarse oxidizer provided the lowest rate of erosive burning. This anomaly was detected by tracking motor pressures versus time for a number of motors shortly after motor ignition, and correlating with precise analytical data for each lot of coarse oxidizer used in the motors (16). Kharetinnov and Boldyrev reported that the number of germs or active sites in AP crystals increased with added AP impurity content. Another factor they noted was that activation energy for nucleation of active sites was determined as being 70 kcal/mol for high purity AP and about 50 kcal/mol for chemically doped AP (9). Thus, lower purity coarse AP oxidizer results in a greater population of active sites and lower activation energies for creating germs that are the source of particle porosity when triggered. High burning propellant exhaust gas velocities adequate for an erosive burning condition provides rapid heat flux to exposed oxidizer particles. High heat flux will set up conditions for quicker oxidizer particle ejection by readily exposing more active sites with lower energies of activation in the less pure oxidizer than for the higher purity oxidizer.

## SUMMARY

AP has odd characteristics not observed in any other oxidizers. One hundred micron sized and larger coarse, AP crystal, thermal decomposition is characterized by formation of highly elongated holes or pores within the crystals (4). These pores emit self-generated decomposition gases. During AP chemical degradation, decomposition gases come both from pore elongation and pore diameter enlargement. Pores extending into AP orthorhombic crystals are always parallel to the principal orthorhombic crystal axis. Extension of principal axis pores into the AP crystals can have length propagating velocities up to ten times faster than expansion of pore diameters (6). Strangely, if AP pores become a major part of action during combustions, recession rates or burn rates within AP crystals will exhibit higher linear velocities parallel to a principal crystal axis as compared to lateral velocities. Such odd behavior might be called differential rate, bidirectional burning. Observations of coarse AP low pressure AP thermal decomposition, AP self-combustion, and AP in burning solid propellants all seem to have pore generation within the AP crystals during the processes. As pressure and temperature environments are increased rate stimulation for pore formation in AP crystals are substantially enhanced.

Under conditions of vacuum to about one atmosphere pressure and temperatures below 240 C, coarse AP pores are formed that grow to some maximum diameter of less than 10 microns where further AP decomposition stops. Pore shapes are not simple cylinders. Ravaeskii's (6) term for pore shapes was "ellipsoids of revolution". During the so called AP low temperature decomposition (LTD), AP samples can lose up to about 30% weight before the process stops. Another oddity of the AP LTD process was that decomposition of AP did not occur until many minutes had passed. Delay period before pore decomposition activation was described as an induction period. Material remaining after AP LTD process stops was quite pure AP that did not decompose further in any sizable amount (4, 6) at temperature below 240 C. AP LTD process residue is highly porous. Porous AP has been referred to as PAP by those trying to use it as a component of solid propellants. Although PAP could produce very high solid propellant burn rates (14), deficiencies for PAP use kept it out of any operational rocket motor system.

Holes formed by limited thermal decomposition of AP crystals originated from about two micron sized cloudy spots within the crystals (4, 6, 8). Spots of unevenly distributed and of varying size were observed to migrate through AP crystals. One micron sized spots were also called "germs" that would slowly join up to form active nuclei. Migration rates were about 10 times faster in a direction parallel to the main AP orthorhombic crystal axis as compared to transverse migration rate. All cloudy spots were found to be associated by ammonium chlorate content in the AP crystals. Since all efforts to remove chlorate ion completely from AP crystals failed, the conclusion was that AP is fundamentally unstable with respect to the formation of minute amounts of chlorate ion in its structure (8).

Chlorate ions cannot move past perchlorate ions in an AP orthorhombic structure with measured activation energies of 31 and 33 kcal/mole depending on migration direction. A suitable mode for chlorate ion migration would be for a chlorate ion to take an oxygen atom from an adjoining perchlorate ion. The original chlorate ion would become a perchlorate ion and the attacked adjacent perchlorate ion would be converted into a chlorate ion removed from the original chlorate ion by one ion width distance. Oxygen atom swapping between chlorate and perchlorate ions would have zero energy for the process since energy consumed for breaking one oxygen atom to chlorine atom bond would be balanced by release of energy produced by formation of one new oxygen atom to chlorine atom bond. Oxygen atom bond swapping is a chemical reaction process. Ten to one difference between parallel to crystal axis migration and transverse migration also indicates, perhaps, an up to a ten to one bias for chemical kinetic reaction rates when burning or consuming coarse AP crystals.

Thom Boggs' AP crystal burning over a wide pressure range had varying results depending upon chamber pressures (11, 12). His AP self-burning trials can be interpreted as involving the characteristic hole forming method of AP decomposition to a more or less degree. Orientation of AP main orthorhombic axis with respect to being either parallel to receding surface direction or orthogonal to receding surface direction may have had an interesting consequence since examination of flame quenched surface should be so different. His observation of quenched crystal burning surfaces having parallel valleys and ridges could have been produced by AP crystal samples where the main AP orthorhombic axis was shifted by 90 degrees from other tests (12, 17). That is, where the main orthorhombic crystal was parallel to the ignited sample surface. This surface configuration could be interpreted as burning surface recession coming sideways to elongated active nuclei in the AP crystals. As active nuclei were stimulated by flame relatively immediate generation of a crosswise burning linear axis (line) could provide a valley as AP burning continued in radial fashion outward from the linear axis producing a rounded valley. Since active nuclei encounters were relatively infrequent, a number of parallel valleys could be produced with ridges left between sideways circular burning zones that would run together. Checking of burn rates for similar sized AP crystal samples where one crystal axial alignment would produce holes and the other with orthogonal axis alignment would produce parallel valleys and ridges would be illuminating. The parallel valleys and ridges sample should have a slower burn surface recession rate than for the other. Parallel ridges and valleys provide support for thought that AP pore forming mechanism was involved in AP self-combustion burns.

Vertical column residues on flame quenched surfaces in Thom Boggs' samples at 1500, 1800, 3300, and 6200 psi have shapes that may have been formed by ignited vertical holes moving faster vertically into AP crystal depths than rate of lateral core burning on interior pore sides. Some columns had curved shapes that could have come from merging pore sidewall burnings. This evidence supports concept of differential rate, bidirectional AP chemical reactions that occurred in spurts during lower pressure trials. In Boggs AP self-burning tests at pressures above 4000 had combustion occurring where AP LTD induction periods were very short. Hole formation burning at these pressure became the



dominating AP burning/decomposition process. Ignition delay periods kept getting briefer as pressures were increased above 4000 psi (11. 12). Growing brevity of induction periods in Boggs' pressure region IV resulted in increasingly higher burn rate pressure exponents with added pressures.

Relatively short term (milliseconds) appearance for 200 micron sized AP particles in a receding HTPB/AP propellant burning surface followed by total disappearance of temporarily exposed large AP oxidizer particles within one millisecond was observed (13). Temporary flame retardancy of exposed AP particles bared by burning propellant recession may contribute to low burn rate pressure exponents and ease of burn rate adjustment by varying AP coarse to fine particle size ratios in AP oxidized solid propellants. Reason for the observed temporary chemical inactivity might be due to the characteristic induction period delay activity noted in lower temperature environments prior to start of AP LTD process. Initial pore forming AP LTD process may be unlikely to be involved during initial heating of coarse oxidizer as particles became exposed in receding burn fronts. A thermomechanical mechanism may have cracked visible particle domes followed by rapid disappearance of oxidizer particles. Since active nuclei would be bared with AP crystal dome cracking, exposed active nuclei could promptly generate a multitude of pores through activated AP particles. With many pores and fractional AP particle conversion to gas products a combination of AP decomposition gases and small AP particulates could be swiftly expelled. Such an expellation of mixed coarse AP products minimally mixed with fuel gases fits as a probable explanation for dark zones between receding HTPB/AP propellant burning surfaces and elevated bright zones where oxidizer and fuel components would become more thoroughly mixed. At relatively low pressures as normally used in solid rocket motor chambers, porosity formation in coarse AP oxidizer particles is inferred to occur once particle dome cracking bares active sites originally within the oxidizer particle.

When low burn rate solid propellants oxidized by AP reach high pressures, typically at some point in 3000 to 5000 psi chamber pressure range for propellants oxidized by 400 and 200 micron sized particles, respectively, relatively abrupt excursions of burn rate pressure exponents takes place. Burn rate pressure exponents up to 1.6 have been observed at pressures above the point of burn rate escalation (slope break). Seventeen micron sized coarse oxidizer propellant did not exhibit a slope break even at 13,000 psi chamber pressure. For 200 micron oxidized solid propellant very high burn rate pressure exponent above 5000 psi chamber pressure is analogous to high burn rate pressure exponents obtained by Boggs at similar pressures. Runaway coarse AP particle porosity forming process may cause AP pocket bottom ignition ahead of normal propellant burn rate recession that could result in high burn rate pressure exponents. For a 200 micron AP oxidized solid propellant burn rates kept increasing with a 1.6 burn rate pressure exponent up to 12,500 psi chamber pressure. When burn pressure exponent at chamber pressures above 12,500 decreased to 0.9, the coarse AP oxidizer particle shattering process must have been saturated so that a more normal burn rate pressure exponent for very high pressures would control the combustion process.

Since porous AP can greatly increase solid propellant burn rates, porous AP can add considerable escalation of eruptive violence of slow cookoff tests on rocket motors filled with AP oxidized solid propellant. Long term durations at elevated temperatures during slow cookoff trials seems disposed to allow formation of porous AP. Over long motor heating cookoff durations, further escalation of explosive violence when thermally abused AP propellant ignited, could be provided by fuel migration to get closer to molecular association with oxidizer.

Erosive burning of AP oxidized solid propellant during stressful parts of a rocket motor firing duration can be enhanced by impurities in coarse oxidizer particles. Added propellant erosive burning

with less pure coarse oxidizer would come from a great proliferation of active nuclei in oxidizer particles and the reduction of activation energy for AP reaction from about 70 kcal/mole for pure AP versus 50 kcal/mole for 99% pure AP.

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